HILGARDIA

A JOURNAL OF AGRICULTURAL SCIENCE

PUBLISHED BY THE

CALIFORNIA AGRICULTURAL EXPERIMENT STATION

Vol. 1 JUNE, 1925 No. 6

THE UTILIZATION OF SULFUR DIOXIDE IN THE MARKETING OF GRAPES

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The rapidly increasing volume of fresh grapes being shipped each year from California often taxes the resources of the railroads severely and during much of the season of 1922 resulted in serious congestion. The condition was similar, though less intense, in 1923. As a result, large quantities of grapes could not be shipped and were left to rot on the vines, while in those shipped, losses from spoiling were much increased by delays in delivery.

In consequence of these losses many inquiries were sent to the College of Agriculture as to methods of bettering these conditions either by improving the efficiency of the refrigerator cars now in use or by employing other modes of transportation.

Several possibilities suggested themselves, all based on the idea of delaying the deterioration of the grapes. This might make it possible to spread the shipments over a longer season, to utilize cars without refrigeration, and to increase the efficiency of refrigerator cars. The capacity of the railroads with their present equipment would thus be increased.

The causes of deterioration in transit or in storage are chiefly evaporation of water from the grapes and consequent shrivelling, and the activity of various micro-organisms causing decay. While on the vine, the grapes are freely exposed to dry air which retards the growth of the micro-organisms, and the water lost by transpiration is replaced by the vine. After removal from the vine, however, the grapes must be prevented from shrivelling by being kept in a relatively moist air to prevent evaporation. Moist air, however, fosters the growth and activity of micro-organisms. The growth of these

organisms can be controlled by sterilization, refrigeration, or chemical preservatives. By sterilization, as in ordinary canning, the conditions of texture, color, and flavor are changed so that the product is no longer fresh fruit. By refrigeration, it is possible to retain the fresh flavor, color, texture, etc., but the time that grapes can be held in this way is limited. Although little is known of the possibility of retarding deterioration of grapes by means of chemical preservatives, the nature of some of these preservatives, together with the positive results they have given in the control of saprogenic (decay causing) organisms in the manufacture of certain fruit products such as cider, grape juice and wines, indicate that it might be possible to prevent the spoiling of fresh grapes for a considerable period by their use.

OBJECT OF THE INVESTIGATION

This investigation is an attempt to determine (1) the possibility of preserving grapes fresh in sealed containers by means of preservatives so that they will be suitable for manufacturing purposes for several months after their removal from the vines and (2) the possibility of retarding spoiling under the present system of refrigerator car transportation, by means of chemical preservatives with a view to placing the grapes on the Eastern markets in better condition.

PRELIMINARY TESTS WITH VARIOUS CHEMICALS

Sulfur dioxide, which has been used successfully for many years as a mean of controlling undesirable organisms in wine making, and various other chemical preservatives, some of which have been used rather widely in fruit and vegetable products, were tested.

In the preliminary tests the grapes were submerged in fresh must containing the various preservatives. The results are in agreement with those obtained by Scott and Will.* Sulfur dioxide was not used by them.

* Scott, R. D., and Will, S. G., Cider Preservatives. Jour. Ind. and Eng. Chem., 13:1141, 1921.

Results Obtained with Various Preservatives

Boric Acid.—In concentrations of from .1 to .15 per cent, boric acid retarded alcoholic fermentation for only a few days. Acetic acid accumulated very rapidly.

Formic Acid.—In the same concentration this acid gave results identical with those obtained with boric acid.

Formaldehyde.—In concentrations of .005 to .0075 per cent, formaldehyde did not retard fermentation.

Benzoate of Soda.—In concentrations of from .1 to .2 per cent, benzoate of soda prevented alcoholic fermentation for several months. The production of acetic acid, which was not inhibited, however, spoiled the grapes in the course of from four to six weeks.

Salicylic Acid.—In concentrations of from .1 to .15 per cent, salicylic acid prevented alcoholic fermentation for from four to six weeks. The production of acetic acid was not retarded.

Sulfur Dioxide.—In concentrations of from .06 to .12 per cent, sulfur dioxide gave indications of controlling both the alcoholic fermentation and the production of acetic acid.

Results very similar to those given above were obtained when the grapes were dipped in solutions of the several preservatives of widely varying concentrations. In these tests again sulfur dioxide alone gave indications of favorable results.

In view of the results obtained in the preliminary tests, all preservatives except sulfur dioxide were soon discarded as unpromising.

SULFUR DIOXIDE (SO_2)

Physical and Chemical Properties.—Sulfur dioxide (SO_2) is a colorless gas, 2.2 times as heavy as air. Its odor, which is very pungent, is characteristic of the fumes produced by burning sulfur. The gas itself will not burn. The gas is soluble in water to the extent of about one part in ten parts of water by weight at room temperature. As a water solution, this substance is known as sulfurous acid. At ordinary atmospheric pressure the gas liquefies at a temperature of —10° C. The liquefied gas is retailed in steel drums, which must be sufficiently strong to withstand considerable pressure, since at 20° C. the gas exerts a pressure of 40.6 pounds to the equare inch.

The gas bleaches organic colors. This action has been widely utilized in the decolorization of walnuts and dried fruits. The gas owes this property to its power of forming colorless compounds by combining with the color chromogens. As a rule, these compounds are easily broken up by oxidation and the color restored. Red grapes can be made white by treatment with SO_2, but on aeration the color returns. In this respect the bleaching action of SO_2 differs from that of other bleaching agents which either destroy or remove the color.

Sulfur dioxide combines readily with certain organic substances found in the grape including the sugars. This combination of SO_2 and sugar is fairly stable and doubtless constitutes a major part of

TABLE 1

THE EFFECT OF SULFUR DIOXIDÉ ON THE MULTIPLICATION OF MICRO-ORGANISMS

Organism*	No. of cells per c.c. at start	Number of living cells per c.c. after 36 hours exposure to the following concentrations. Milligrams of sulfur dioxide per liter				
		None	50	100	200	400
Wine Yeast	20,000	....	640,000	2,000,000	310,000	36,000
Apiculatus	150,000	....	200,000	75,000	56,000	0
Wild Yeast (Pastorianus form.)	620,000	....	580,000	6,000	190	0
Penicillium	120,000	....	40,000	0	0	0
Aspergillus	450,000	....	120,000	20,000	30,000	0
Vinegar Bacteria	310,000	610,000	14,000	300	2	0

* All of these organisms except the wine yeast were isolated from California grapes.

the combined SO_2 in the treated grapes. When grapes are treated with SO_2, there is also a portion of the gas that does not enter into any combination. It is this portion which is usually termed *free* SO_2. It is to the free SO_2 that the retardation or prevention of spoiling is due, since in this form it is a very active preservative.

The Retarding Effect on the Growth of Saprogenic Organisms.—Spoiling of grapes in storage or transit is due primarily to the activity of molds, yeasts, and bacteria. Of the molds, types of Penicillium, Aspergillus, Botrytis, Mucor, and Monilia are the most common. Of the yeasts, the true wine yeast (*Saccharomyces ellipsoideus*), the wild yeasts (forms of *S. pastorianus* and *S. apiculatus*), and the pseudo yeasts, Mycodermae, are the most common. The bacteria usually met with are forms producing vinegar.

The growth of all of these organisms is retarded or prevented by SO_2 in sufficient concentration. The effect of different concentrations of SO_2 on the multiplicaton of some of these organisms as observed by Cruess* is shown in table 1. Chabert† found that visible active fermentation of grape must was retarded by the addition of small quantities of sulfur dioxide. His observations are given in table 2.

The Effect on the Metabolism of Grapes.—Sulfur dioxide in addition to controlling or inhibiting the growth and activity of micro-organisms effects a slowing up in metabolic changes, e.g., the respiration which normally occurs in grapes. Tests were made in duplicate

TABLE 2

THE EFFECT OF SULFUR DIOXIDE IN RETARDING VISIBLE FERMENTATION

Concentration of SO_2		Time that visible fermentation was retarded	
Milligrams per liter	Per cent	Ordinary temperature (presumably 20° C.)	28° C.
10	0.001	Appreciably	....
30	0.003	10–12 hours	....
50	0.005	18–21 hours	6 hours
75	0.0075	48–60 hours	....
100	0.01	5–6 days	32 hours
150	0.015	....	97 hours
200	0.02	....	146 hours
250	0.025	....	More than 8 days

with treated and normal grapes in order to determine the rate at which carbon dioxide is liberated. As shown by the graphs in figure 1, the slowing up in the release of carbon dioxide is positive and for amounts less than 300 mgs. per kilo. of grapes is more or less proportional to the amount of sulfur dioxide applied. The figures plotted here were obtained with Grenache which had a sugar content of 26 degrees Balling.

It is of interest to note the uniform slope of the several graphs in figure 1. The effect of the SO_2 seems to be confined to the life processes of the grape with little or no destruction of the tissue. The variations in the individual determinations were a result of the fluctuating temperature in the laboratory.

* Cruess, W. V., The effect of H_2SO_3 on fermentation organisms. Jour. Ind. and Eng. Chem., 4:581–585, 1912.

† Chabert, F., Prog. Agr., 37:574–579, 1892.

SULFUR DIOXIDE IN THE PRESERVATION OF GRAPES IN SEALED CONTAINERS*

The object in mind in making these tests was that of devising means, if possible, whereby grapes intended for grape juice or other grape products could be packed and preserved for temporary storage or shipment without refrigeration and without elaborate equipment or great expense. A method capable of this would not only enable the growers of grapes for manufacturing purposes to dispose of their

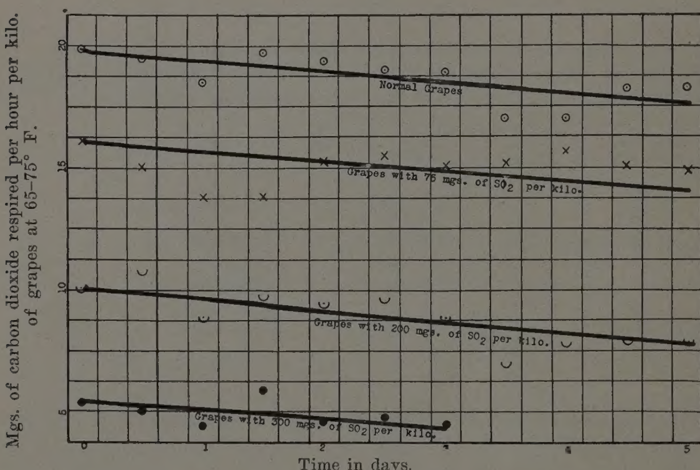

Fig. 1. The effect of SO_2 on the rate of respiration in grapes.

entire crop more readily, but might also release a considerable number of refrigerator cars for the handling of our increasing tonnage of table grapes.

Sulfur dioxide has been used for years to hold crushed grapes (must) in temporary storage during the rush season of harvesting.

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* Some tests were made by F. T. Bioletti on the preservation of fresh grapes in sealed containers containing atmospheres of SO_2, CO_2, alcohol vapor and air. These were reported in the Report of the Vit. Work of the Coll. of Agr., Univ. of Calif., **1896**, 447–450.

Some preliminary tests on the shipping of grapes in closed barrels were reported by F. T. Bioletti in the California Grape Grower, vol. 5, August, 1924. In these tests the Grape Growers Exchange, the Sun Maid Raisin Growers Association, and the California Barrel Company were coöperating with the College of Agriculture of the University of California.

In European countries it has also been used to retard fermentation in short distance shipments of must and grapes from the vineyards to the wineries. Impetus was given to these tests by the landing in New York of Italian grapes in barrels during the latter part of the 1922 season. Although not entirely successful, these shipments of

TABLE 3

THE RETARDING EFFECT OF SULFUR DIOXIDE ON THE SPCILING OF GRAPES IN SEALED CONTAINERS AS INDICATED BY SUGAR CONTENT

Variety	Mgs. of SO_2 per kilo. of grapes	Balling degree of the expressed juice						
		At the beginning	After 1 month	After 2 months	After 3 months	After 4 months	After 5 months	After 8 months
Series A								
Valdepeñas	0	23.	0 After 10 days					
	350*	23.	0 After 20 days					
Alicante Bouschet	0	22.5	0					
	300*	22.5	15.7					
	300*	22.5	17.5	3.8	0.1			
	600*	22.5	19.2	18.8	15.4	17.5		
Malaga	0	22.5	0					
	600*	22.5	19.6	18.4			21.2	
Series B								
Cornichon	0	18.4	0					
	600†	18.4	17.6	18.1			18.7	4.5
	900†	18.4					19.8	14.4
	650‡	18.4	16.9	16.5			19.3	
	900‡	18.4			18.6		20.4	
	650§	19.0	16.2	16.4		1.5		
Series C								
Tokay	0	20.4	0					
	900†	20.4	20.1	19.0	20.8	20.3	20.8	
	650†	20.8	18.7	18.6	20.7	20.4	20.3	
	550†	20.5	18.4	18.4	19.4	19.5	19.5	
	800†	21.3	22.1	21.6	21.6	20.4	20.7	

* SO_2 applied in a small amount of water.
† SO_2 applied by immersion.
‡ SO_2 applied as gas.
§ SO_2 applied in must.

Italian grapes indicated that, with a sufficient knowledge of all the factors concerned, the sugar content of grapes might be retained almost indefinitely.

Retardation of Spoiling.—Although it is recognized that the free rather than the combined SO_2 is primarily responsible for the effect

on micro-organisms, only the total SO_2 present in the grapes will be considered in this discussion, since it is obviously impossible to control the relative amounts of free and combined SO_2 in the filled containers. It should, however, be borne in mind that there is a more or less direct relation between the free and the total amount of SO_2 present.

TABLE 4

THE RETARDING EFFECT OF SULFUR DIOXIDE ON THE SPOILING OF GRAPES IN SEALED CONTAINERS AS INDICATED BY THE ACCUMULATION OF ALCOHOL

Variety	Mgs. of SO_2 per kilo. of grapes	Per cent of alcohol present						
		At the beginning	After 1 month	After 2 months	After 3 months	After 4 months	After 5 months	After month8
Series A								
Valdepeñas	0	Trace	Moldy after 10 days					
	350	Trace	Moldy after 10 days					
Alicante Bouschet	0	Trace	11.55	....	....	....		
	300	Trace	1.92	9.0	....	....		
	300	Trace	1.02	8.8	9.1	....		
	600	Trace	0.35	0.75	0.75	0.83		
Malaga	0	Trace	9.1	....	....	....	....	
	600	Trace	Trace	Trace	....	....	0.2	
Series B								
Cornichon	0	Trace	7.8	....	....	....	....	....
	600	Trace	0.17	0.19	....	....	0.29	6.2
	900	Trace	....	....	....	....	0.2	1.1
	650	Trace	0.23	0.37	....	....	0.19	....
	900	Trace	....	....	0.18	....	0.27	....
	600	Trace	0.25	0.18	....	7.5	....	....
Series C								
Tokay	0	0.25	Completely spoiled after 13 days					
	900	0.3	0.3	0.3	0.3	0.3	0.3	
	650	0.2	0.2	0.2	0.2	0.2	0.2	
	550	0.2	0.2	0.2	0.2	0.2	0.4	
	800	0.25	0.3	0.3	0.3	0.2	0.3	

To obtain data on the efficiency with which spoiling could be controlled in grapes in sealed containers, several series of jars, kegs, and barrels filled with grapes were treated with varying amounts of SO_2. The amount and manner of applying the SO_2 and the results from representative containers with regard to loss in sugar content and the accumulation of alcohol are given in tables 3 and 4.

An examination of tables 3 and 4 reveals that 300–400 mgs. of SO_2 per kilo. of grapes is insufficient to successfully retard the spoiling of grapes in sealed containers. Although spoiling was retarded from four to six weeks in some containers, others under similar conditions kept little better than the untreated checks. This wide variation in the results obtained in these tests indicates that 300–400 mgs. is below the minimum required for practical purposes to preserve grapes.

By increasing the amount of SO_2 to 600 mgs. per kilo., it was possible to retain nearly the entire sugar content of the grapes and to suppress the accumulation of alcohol for from four to six months. The efficiency with which SO_2 at this concentration preserved the grapes in sealed containers is best illustrated by the results obtained under series B and C as shown in the above tables. These series were carried out after some of the difficulties which resulted in early spoiling, e.g., lack of uniformity in the distribution of the SO_2, leaky containers, etc., in series A, had been discovered and special efforts made to overcome them.

Again, by increasing the amount of SO_2 to 800–900 mgs. per kilo. it appears that the loss of sugar and the accumulation of alcohol may be retarded almost indefinitely. At present (March, 1925) grapes have been held for eight months under these treatments with little or no variation in the sugar and alcohol contents.

Importance of Uniform Distribution.—The results of the first tests made with SO_2 in sealed containers varied greatly. Analysis of the methods used in applying the preservative and of the results obtained indicated that this variation in the behavior of lots treated in a similar manner was due chiefly to lack of uniform distribution of the preservative throughout the grapes.

Table 5 shows the behavior of three representative units of each of three series. One unit, barrel No. N. 39, treated with approximately 300 mgs. SO_2 per kilo. of grapes still gave a sugar test of 11 degrees Balling six months after treatment; while another unit, barrel No. N. 44, treated with 600 mgs. per kilo., showed practically no sugar at the end of six months. The entire "D" series of Malaga grapes, three representative units of which are shown in table 5, treated with approximately 600 mgs. of SO_2, gave very uniform results.

Table 6 shows an analysis of one of each of these three series. The two series of Alicante Bouschet represented by barrels Nos. N. 33, 34, and 39, and N. 43, 44, and 49 treated with 300 mgs. and

TABLE 5

VARIATION IN THE BEHAVIOR OF VARIOUS BARRELS

Barrel	Size of barrel in gallons	Variety	Approximate SO_2 added in mgs. per kilo.	Period of storage	Balling degree
N. 33	10	Alicante Bouschet	300	1 month	15.7
N. 34	10	Alicante Bouschet	300	6 months	0.
N. 39	10	Alicante Bouschet	300	6 months	11.0
N. 43	10	Alicante Bouschet	600	1 month	19.4
N. 44	10	Alicante Bouschet	600	6 months	0.5
N. 49	10	Alicante Bouschet	600	6 months	13.5
D. 9	10	Malaga	600	1 month	19.6
D. 10	10	Malaga	600	2 months	18.4
D. 11	10	Malaga	600	6 months	21.2

TABLE 6

VARIATIONS IN DIFFERENT PARTS OF THE SAME BARREL

	SO_2 content mgs. per kilo.	Balling degree	Alcohol content in per cent
Keg Number N. 33, Alicante Bouschet after 1 month:			
Grapes near top of keg	164	19.7	0.95
Grapes near center of keg	45	14.5	2.96
Grapes near bottom of keg	365	18.5	0.98
Keg Number N. 43, Alicante Bouschet after 1 month:			
Grapes near top of keg	393	22.8	0.26
Grapes near center of keg	75	17.3	1.2
Grapes near bottom of keg	470	18.8	0.21
Keg Number D. 11, Malaga after 6 months:			
Grapes near top of keg	395	19.8	0.28
Grapes near center of keg	384	22.0	0.21
Grapes near bottom of keg	574	21.7	0.13

600 mgs. SO_2 respectively show a relatively high concentration of SO_2 at the bottom of the barrel, a lower concentration at the top and a very low concentration at the center of the barrel. Because of this low concentration of SO_2 in the center of the barrel there was a correspondingly low sugar and high alcohol content in grapes in this part of the container. Barrel No. D. 11, representing a series of Malaga treated with approximately 600 mgs. of SO_2 per kilo., shows a very

much more uniform distribution of SO_2 throughout the grapes and after six months the sugar content and alcohol content were practically the same as when treated. To prevent spoiling, the concentration of SO_2 in the grapes in all parts of the container must be sufficiently high to prevent the growth of micro-organisms.

Relation of Type and Size of Container to Efficiency.—In these tests three types of containers were used:

1. Glass containers of several sizes and several methods of sealing.
2. Metal cans of about 5 gal. capacity. These cans were coated with paraffin on the inside to prevent corrosion of the metal by the acids of the grapes and the SO_2.
3. Wooden kegs and barrels. These were of four sizes, 4 gal., 10 gal., 25 gal., and 50 gal. Some were plain fir kegs, some were paraffin lined, some asphalt lined and others were coated with paraffin on the outside after filling.

The behavior of the grapes in these various types and sizes of containers was comparable so long as the distribution of the SO_2 was uniform throughout the grapes in the container, and so long as the container itself remained air tight. Difficulty was experienced with the drying out of the plain wood kegs so that they ceased to be air tight, but except for this there was no difference in any of the experiments that could be attributed to the type or size of the container. Under similar conditions with similar uniform concentration of SO_2 the grapes kept equally well in 50-gallon wooden barrels and 2-quart glass preserving jars.

Relation of the Form of the Sulfur Dioxide to Efficiency.—The sulfur dioxide was applied to the grapes in three forms, namely, as sulfurous acid (H_2SO_3), as potassium or sodium metabisulfite ($K_2S_2O_5$ or $Na_2S_2O_5$) and as the gas (SO_2).

The sulfurous acid and potassium or sodium metabisulfite were brought into contact with the grapes in the following ways: (1) by submerging the grapes in the containers in must which carried the desired amount of the preservative; (2) by immersing the grapes in the container for a definite period of time in a suitable water solution of the preservative; and (3) by transferring the desired amount of the preservative to the filled container of grapes with a small amount of water.

Immediately after the treatments by immersion and by the addition of the preservatives with a small amount of water, the kegs or barrels were rolled and turned end over end in order to bring the solution into contact with as many of the individual berries as possible. This facilitated uniformity of distribution in the container,

since the sulfur dioxide is rapidly absorbed by the berries in contact with the solution.

The sulfur dioxide as a gas was brought into contact with the grapes directly. The gas was diluted with air in accordance with the concentration of SO_2 desired in the grapes and was then forced to flow rapidly through the filled containers of grapes for a definite period of time.

With less than 1000 mgs. per kilo. all lots treated by submerging the grapes in must to which the preservative was added in the form of sulfurous acid or potassium or sodium metabisulfite fermented in from 1 to 4 months. Series B, Cornichon, table 3, page 113, shows the results obtained in one lot treated with 650 mgs. SO_2 per kilo. in this manner. Treatments by the other methods, viz., (*a*) immersing the grapes in the container for a definite period of time in a suitable water solution of the preservative, (*b*) by transferring the desired amount of the preservative to the filled containers of grapes in just enough water to wet all the grapes in the container, (*c*) by exposing the grapes in the container to a definite concentration of SO_2 as a gas for a definite length of time, all gave equally good results, *whenever a uniform application was obtained.* It was difficult and uncertain, however, to obtain a uniform application by applying the preservative in just enough water to wet the grapes in the container, and this is therefore not a method to be recommended.

All lots of grapes treated by immersion or by gas as described, in which the amount of the preservative added was 600 mgs. per kilo. or more, retained practically all their original sugar content and showed no activity of micro-organisms for at least four months after treatment. Analyses of six of these lots in series B and C are given in tables 3 and 4.

Condition of the Grapes after Storage.—By suppressing the activity of micro-organisms the loss of sugar and the accumulation of alcohol were prevented. An effect of the SO_2 on the grapes, however, was to increase the permeability of the cells of all parts of the fruit and stems. The color was released from the skins, and the tannins and other substances from the seeds and stems. The berries showed varying amounts of "leakage" so that some free juice accumulated in the container. The appearance and condition of the fruit was decidedly not "fresh" and in no case would it be suitable for table fruit. For manufacturing purposes where the release of the color and tannins and other substances into the juice is not objectionable the grapes were nearly equal to fresh fruit. The color is temporarily bleached by the SO_2 but returns as soon as the preservative is removed.

SULFUR DIOXIDE IN THE PRESERVATION OF GRAPES IN OPEN CONTAINERS

Grapes have been ''sulfured'' by burning sulfur in the cars after loading for shipment to distant markets, at sporadic intervals for some eight or ten years. In the main these ''sulfured'' grapes have reached the markets in no better condition than the untreated shipments and in many instances their quality was impaired. In a few instances they have arrived on the distant markets in excellent condition. Adequate checks, however, have been lacking in all cases.

In the early work on the preservation of grapes in sealed containers, certain results obtained in tests on the rate of absorption of SO_2 by the grapes and the rate at which it was lost later when the grapes were exposed to laboratory conditions indicated that it might be possible to retard spoiling in open containers for a period of several days to several weeks. In the light of these results together with the fact that ''sulfured'' grapes have sometimes been shipped with partial success, tests were started in 1923 and continued with considerable elaboration in 1924, with a view of improving the method of application so that uniformly good results might be obtained.

Rate of Absorption by Grapes

SO_2 as a gas, when brought into contact with grapes, is readily absorbed by them. The rate of absorption of the SO_2 is influenced by the concentration of SO_2 in the atmosphere, the time of exposure, and by the temperature, maturity, and physical condition of the grapes.

Influence of Concentration and Time of Exposure.—Since the data on the relation of the concentration of the SO_2 and the time of exposure on the rate of absorption of the gas by the grapes were collected in the same tests they are presented together. Varying concentrations of SO_2 in air were forced over grapes in glass cylinders for given periods of time. The concentration of the SO_2 in the atmosphere was determined by absorption in iodine both before and after passing over the grapes. After the given time of exposure, representative samples of the grapes in the cylinders were removed and analyzed for SO_2. Representative results for several concentrations of SO_2 at the shorter periods of treatment are given in table 7.

The figures of table 7 show that at relatively low concentrations, the SO_2 is absorbed very rapidly from the atmosphere. The figures further indicate that the concentration of the gas as well as the time of treatment must be capable of careful control, and that the concentration of SO_2 must be uniform throughout the car. Only a small variation in the concentration of the SO_2 or the time of exposure may result either in too low a concentration of SO_2 in the grapes to suppress the activity of the micro-organisms or in a concentration sufficiently high to seriously injure the flavor and texture of the fruit.

TABLE 7

THE INFLUENCE OF THE CONCENTRATION OF SO_2 AND OF THE TIME OF EXPOSURE ON THE RATE AT WHICH THE GAS IS ABSORBED BY GRAPES

Variety	Per cent of SO_2 in the atmosphere	Mgs. of SO_2 per kilo. absorbed			
		In 10 minutes	In 20 minutes	In 30 minutes	In 40 minutes
Valdepeñas	0.5	....	....	....	165
Muscat	2 to 3	60	85	114	
Tokay	2 to 3	58	64	93	
Muscat	4 to 6	99	251	656	
Tokay	4 to 6	70	171	547	

Influence of Temperature of the Grapes.—In these tests the range of temperatures occurring in practice was covered. The SO_2 gas was forced over the grapes in glass cylinders at the several temperatures. Uniformity of treatment was obtained by supplying the same volume of gas of the same concentration to all the cylinders at the same time. The volume of SO_2 supplied was very much greater than that absorbed by the grapes. The results obtained are shown in figure 2.

The graph of figure 2 shows that within the small range of temperatures usually met with in a car the matter of temperature of the grapes is of less importance than the concentration of the SO_2 or the duration of the treatments. There is, however, a direct relation between temperature and the rate of absorption; hence, where the temperature varies considerably as it may between cars at different seasons or in different localities, it must be taken into account in order to obtain uniform results.

Influence of Maturity of the Grapes.—This was determined by exposing grapes of various degrees of ripeness to a known concentration of SO_2 for a given period of time. The data shown in table 8 were obtained.

The figures of table 8 clearly show the necessity of having grapes of uniform ripeness where uniformity of treatment is desired. By varying the ripeness, as indicated by the Balling test, five degrees (from 18 to 13 in case of Muscat) the amount of SO_2 absorbed was more than tripled.

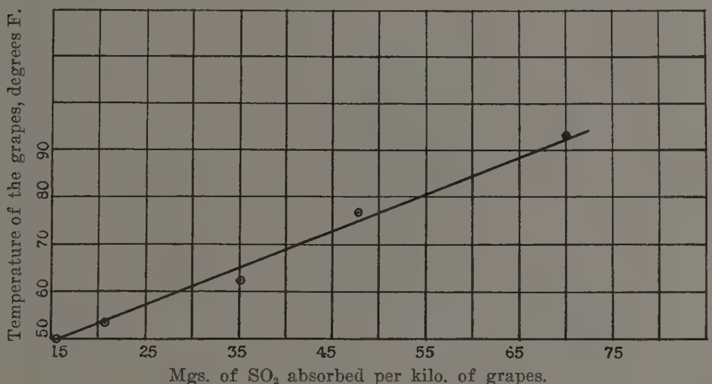

Fig. 2. The influence of the temperature of the grapes to the rate of SO_2 absorption.

TABLE 8

THE INFLUENCE OF MATURITY OF THE GRAPES TO THE RATE OF ABSORPTION OF SO_2

Variety	Mgs. of SO_2 absorbed per kilo. of grapes*		
	Ripe	Green	Very green
	(27° Bal.)	(18° Bal.)	(13° Bal.)
Muscat	43	77	262
	(23° Bal.)	(17° Bal.)	(10° Bal.)
Cipro Nero	110	129	218

* Treated for 7 minutes with a mixture of 4 per cent of SO_2 in air.

Influence of Condition (Soundness) of the Grapes.—Since the growth of micro-organisms and therefore the spoiling of grapes starts readily in injured berries, it is of particular interest to determine the rate and amounts of SO_2 absorbed by these berries as compared with sound grapes. To obtain data on the relation of injury to the rate at which the SO_2 is absorbed, a considerable number of Tokay and Muscat berries were carefully stemmed in such a way as to confine the extent of the injury to the removal of the stems. Stemmed

berries and sound bunches of these varieties were then treated in identical fashion with regard to SO_2 concentration, air flow, and time of exposure. The results obtained are given in table 9.

The figures of table 9 show that stemmed berries absorbed SO_2 approximately twice as rapidly as sound berries. This more rapid intake of SO_2 by the injured fruit offers additional opportunity for getting the greatest possible retardation of spoiling by a minimum application of the gas. As spoiling usually starts in the injured berries, its arrest at this point through the absorption of larger amounts of SO_2 will largely remove the danger of spoiling in the sound grapes.

TABLE 9

THE INFLUENCE OF PHYSICAL CONDITION (SOUNDNESS) OF THE GRAPES ON THE RATE AT WHICH SO_2 IS ABSORBED

Variety	Condition of berries	Mgs. of SO_2 per kilo. absorbed from 2 to 3% in air		
		In 10 minutes	In 20 minutes	In 30 minutes
Muscat	Sound	60	85	114
	Stemmed	121	154	211
Tokay	Sound	58	64	93
	Stemmed	105	144	200

Application to Grapes in Open Containers.—In making these tests the conditions of the experiment were made as nearly as possible identical with those prevailing in an ordinary refrigerator car. Two air-tight rooms, each of approximately ¼ the size of a car, were used for the treatment and storage of the grapes. One of these rooms was equipped with an ice compartment for refrigeration so that the temperature could be maintained at 50° to 55° F. The other room was ventilated but not refrigerated. Both rooms were provided with floor racks.

The grapes were packed in Standard No. 1 (Los Angeles) lugs in the usual manner of "jumble pack." These lugs were not lidded and were stacked in the rooms in a manner similar to that used in the loading of a car, leaving spaces between the rows lengthwise of the room so as to permit the circulation of air horizontally and vertically.

The SO_2 was applied to the grapes in two ways: (1) By immersing the boxes filled with grapes in a solution of potassium metabisulfite of definite concentration for a definite period of time (see table 10, test no. 1); (2) as a gas.

The SO_2 for the gas treatments was produced by burning sulfur (1) in a specially constructed stove provided with a forced draft (see table 10, tests Nos. 2 and 3), and (2) in the closed rooms (see p. 128).

The special stove for the rapid generation of SO_2 by burning sulfur is shown in figure 3. It consisted essentially of an air-tight outside shell, constructed of thin sheet iron and concrete, into which

Fig. 3. Stove for the rapid burning of sulfur. Note the multiple pan burner and the fan for forced draft.

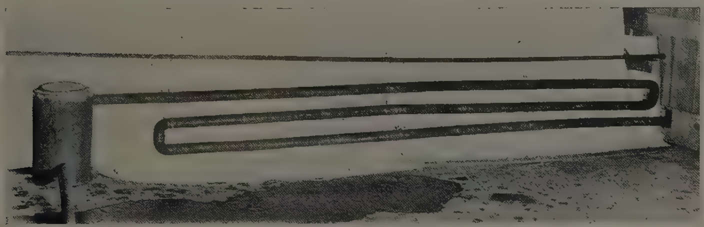

Fig. 4. Coil for cooling gas. Holes in the lower side of the pipe which supports the coil permitted the playing of cold water on all parts of the coil continuously.

was fitted an inlet at the bottom, an outlet at the top, and a tight fitting lid which could be opened so that the burner could be taken out and recharged. The burner consisted of an iron rack on which could be placed, in position one above the other, from one to five shallow pans filled with sulfur. This burner is similar to an arrangement recommended by the Gulf Sulphur Company for the rapid burning of sulfur. A forced draft was obtained by connecting the discharge of an electric vacuum cleaner fan with the inlet to the stove.

Under this forced draft the sulfur burned vigorously, the heat from the lower pans vaporizing the sulfur in the upper pans. With this multiple pan burner, the concentration of SO_2 in the gas from the stove could be varied from 1 to 5 per cent by varying the number of pans used in the burner. The hot gas was cooled before being driven into the room where the grapes were placed, by carrying it through a long pipe over which a stream of cold water was kept running (see fig. 4). Some of the results obtained in these experiments are given in table 10.

TABLE 10

THE RELATION OF MANNER OF APPLICATION TO THE UNIFORMITY OF DISTRIBUTION OF SO_2 IN GRAPES WHEN STORED IN BULK AND THE EFFICIENCY WITH WHICH SO_2 RETARDS THE SPOILING OF GRAPES IN OPEN CONTAINERS.

Test No. and varieties	Average temperature of room	Position of the samples in the room			Mgs. of SO_2 absorbed per kilo. of grapes	Days elapsing before spoiling
		Stack	Row	Layer		
Test No. 1[1] with Sultanina.	76° F.	1	1	1	190	13 days
		1	3	6	78	10 days
		3	2	3	135	12 days
		5	1	6	74	10 days
		3	1	1 to 6	0 (check)	5 days
		2	2	1 to 6	48[3]	9 days
Test No. 2[2] with Muscat and Tokay.	74° F.	3	1	1 to 6	0 (check)	5 days
		5	3	6	80	15 days
		4	1	1	102	15 days
		4	1	4	99	15 days
		3	2	3	85	15 days
		2	1	2	90	15 days
		2	3	4	91	15 days
		1	1	6	91	15 days
		1	3	1	80	15 days
		5	1	1 to 6	0 (check)	5 days
Test No. 3[2] with Muscat and Tokay. (Grapes in poor condition, many broken berries.)	55° F.	3	1	1 to 6	0 (check)	7 days
		1	3	4	269	More than 18 days
		2	1	3	243	More than 18 days
		2	3	6	265	More than 18 days
		3	1	1	249	More than 18 days
		3	2	5	272	More than 18 days
		4	2	3	275	More than 18 days
		5	1	1	240	More than 18 days
		5	3	5	256	More than 18 days
		1	3	1 to 6	0 (check)	7–8 days

[1] Only one large pan used.
[2] Stove with multiple pan burner.
[3] Immersed for one minute in a 7% solution of potassium metabisulfite.

The outstanding facts brought out by the data of table 10 are: (1) that uniformity of distribution of SO_2 can be obtained when grapes are treated in air-tight rooms in which the arrangement of the boxes is similar to that of a loaded car, and (2) that grapes uniformly treated with the proper amount of SO_2 as a dry gas may be expected to keep at least twice as long as the untreated checks when held under the same conditions of storage. These statements are borne out by the figures obtained under tests nos. 2 and 3 as well as by those of the samples taken from and the returns obtained on a treated car which are reported on page 130.

Treatment by immersing the grapes in a water solution of potassium metabisulfite although resulting in a uniform distribution of SO_2 was not so effective in retarding spoiling as treatment with the gas, and the wet condition of the grapes after treatment detracted considerably from their appearance.

Uniformity of Distribution.—The fact that a uniform distribution of SO_2 in the room or car can be obtained when the SO_2 is applied in the proper manner is brought out in table 10, tests nos. 2 and 3 (also in the treated car reported in table 13).

The lack of uniform distribution in test no. 1 was the result of inadequate SO_2 supply rather than a fault of the method of application. In this test it required a considerable period of time (35 minutes) to burn the required amount of sulfur; hence, the displacement of the air in the room with the SO_2 air mixture was very slow and the grapes near the place of entry of the gas absorbed the greater amounts. In this case the sample from layer 1, row 1, and stack 1 with 190 mgs. SO_2 was directly in front of the gas inlet, while the sample from layer 6, row 1, and stack 5 with 74 mgs. SO_2 was from the part of the room farthest from the inlet.

In test no. 2, however, where the necessary sulfur was burned in less than ten minutes, the displacement of the air in the room with the SO_2 air mixture was very rapid and complete; thus all the grapes were exposed to an SO_2 air mixture of about the same concentration for the same length of time, which resulted in a nearly uniform absorption of gas by the grapes in all parts of the room. Here the sample, layer 1, row 3, stack 1, from directly in front of the inlet absorbed 80 mgs. SO_2, the same amount as that absorbed by the sample from layer 6, row 3, stack 5, from the farthest part of the room. Furthermore, the variations which did occur in the amounts of SO_2 absorbed by grapes from different parts of the room in tests nos. 2 and 3 were found to be the result of variation in the condition

of the grapes such as Balling degree, injury, etc. (See pp. 121 and 122).

Retardation of Spoiling.—The data of table 10 indicate that only a relatively small amount of SO_2 need be absorbed by the grapes greatly to prolong their period of utility. In test no. 1, the treatment was not uniform and most of the grapes contained less than 100 mgs. of SO_2 per kilo., and yet they kept twice as long as the untreated check. The grapes of test no. 2, which received a very uniform treatment of from 80 to 100 mgs. of SO_2 per kilo., kept three times as long as the checks.

The question might arise as to why the checks spoiled so rapidly (5 days) in these tests. This is accounted for by the high temperatures of the storage rooms, which were 76° and 74° F. respectively.

In test no. 3 reported in table 10 the grapes were purposely injured through careless picking and through the transfer from field lugs to standard no. 1 lugs in order to see how this might influence the amount and uniformity of distribution of the SO_2 absorbed and the time elapsing before spoiling. A better idea of the condition of these grapes may be obtained by considering the fact that the untreated checks spoiled completely in seven days at 55° F. The SO_2 treatment given these grapes was identical with that of test no. 2 as regards concentration and duration. In test no. 3 the condition of the grapes, however, was such as to hasten the rate of SO_2 absorption (see table 9); hence, the amount absorbed was three times as much as that absorbed by the sound grapes of test no. 2. In spite of the poor condition at the time of treatment, these grapes kept nearly three times as long as the untreated checks.

Effect of Varying Amounts on Keeping Quality, Color, Texture, and Flavor.—In the application of SO_2 to table grapes or to any fruit of which the appearance greatly affects the sale value, the effect of the preservative on color, texture, and flavor must be considered as well as the retardation of spoiling.

To obtain information on the effect of varying amounts of SO_2 on the condition of the grapes and on the retardation of spoiling, grapes were carefully packed in large glass containers and then treated with varying amounts of the preservative. After the treatments, samples for analysis were removed for determining the exact amounts of SO_2 absorbed and the condition of the grapes of each container. The containers were then covered with cheese cloth to exclude vinegar flies and held at room temperature until spoiling occurred. The glass container permitted frequent observation of color and spoiling with-

out disturbing the pack. The effects on flavor and texture were determined by examining and tasting samples removed from the container from time to time. The results of these tests are shown in table 11.

TABLE 11

THE EFFECT OF VARYING AMOUNTS OF SO_2 ON KEEPING QUALITY, APPEARANCE AND FLAVOR OF GRAPES

Variety	Mgs. of SO_2 per kilo. added to the grapes	Color and texture of treated grapes	Days elapsing before spoiling	Effect of the SO_2 on flavor
Black Prince	0 (check)		7 days	
	64	Normal	16 days	Flavor normal
Cipro Nero	0 (check)		6 days	
	46	Normal	13 days	Flavor normal
	70	Normal	20 days	Flavor normal
Malaga	0 (check)		8 days	
	35	Normal	14 days	Flavor normal
	92	Normal	16 days	Flavor normal
	201	Normal	20 days	Stale after 20 days. Trace of SO_2 in taste.
	451	Color lighter. Somewhat soft	25 days	SO_2 taste pronounced
Hunisa	0 (check)		8 days	
	19	Normal	11 days	Flavor normal
	38	Normal	14 days	Flavor normal
	185	Normal	20 days	Taste slightly injured
	454	Pale rose color Somewhat soft	25 days	SO_2 taste pronounced
Ohanez	0 (check)		10 days	
	13	Normal	16 days	Flavor normal
	43	Normal	22 days	Flavor normal
	125	Normal	30 days	Taste almost normal after 30 days
	256	Normal	30 days	Trace of SO_2 in taste

The data of table 11 indicate that about 50 mgs. of SO_2 per kilo. of grapes is sufficient to double the keeping period and that 100 mgs. does not injure the color, texture, or flavor of the varieties used in these tests. In view of these results it appears that the proper amount of SO_2 to apply to table grapes to delay spoiling in transit or storage is from 50 to 100 mgs. per kilo. of grapes.

Application by Burning Sulfur Inside the Closed Room.—Most of the "sulfuring" of loaded cars of grapes that has been attempted in the past has been done by burning sulfur inside the car after the doors have been closed. To test the efficiency of this method several experiments were set up in the tight rooms mentioned.

Burning the sulfur in open pans. In one set of these experiments an effort was made to generate the SO_2 by burning the sulfur in open pans inside the room. The grapes were packed and placed in the room as described on page 122. Three shallow pans, each containing from 1½ to 2 pounds of sulfur were placed side by side on the floor and ignited. The door and ventilators were closed. The results obtained in the most successful of this set of experiments are given in table 12.

TABLE 12

THE AMOUNT OF SO_2 ABSORBED BY GRAPES WHEN THE SULFUR WAS BURNED IN OPEN PANS IN A CLOSED ROOM*

Number of treatment	Pounds of sulfur burned	SO_2 concentration in grapes. Mgs. per kilo. after each successive treatment			SO_2 absorbed at each treatment (average)
		Minimum	Maximum	Average	
First	1.01	23	35	26	26
Second	1.8	....	....	60	34
Third	1.8	72	144	114	54

* The size of this room was about ½ the size of an ordinary refrigerator car.

It required three successive treatments to obtain over 72 mgs. of SO_2 per kilo. of grapes. The first application, in which a little over 1 pound of sulfur was burned, gave an average of only 26 mgs. per kilo. The second application, in which 1.8 pounds of sulfur were burned, gave only 34 mgs. per kilo. The successive treatments raised the temperature of the room considerably, so that the third treatment resulted in a somewhat greater increase in concentration (54 mgs. per kilo.).

When sulfur is burned inside an air-tight room, the oxygen content of the air is soon reduced below the concentration necessary to support combustion, and although a total of over 4½ pounds of sulfur was placed on the pans in the room not more than 1.8 pounds burned.

The data of this table also show that the distribution of SO_2 was not uniform, varying from 144 mgs. per kilo. near the burning sulfur to 72 mgs. per kilo. in another part of the room.

Results similar to these were obtained when the sulfur was placed in pans, one above the other, in the rack used in the burner for the stove discussed on page 123.

Burning the sulfur in a stove placed inside the room. By placing the stove described on page 123 inside the room, with the lid of the stove removed and the draft inlet connected to the air outside of the room and with the ventilators of the room open, more sulfur was burned, so that the required concentration of SO_2 in the grapes was obtained by one treatment. A forced draft was not used in these tests. However, the uniformity of distribution was no better and the heat produced by the burning of the sulfur raised the temperature of the grapes as much as 25° F. This excessive increase in temperature caused the treated grapes of these tests to spoil almost as soon as the untreated checks of other experiments. In the refrigerated rooms, it required several days to reduce the temperature to 60° after treatment in this manner.

Shipment of a Car-Load of Treated Grapes.—Through the cooperation of Mr. J. H. Wheeler of St. Helena, California, we were enabled to obtain samples for analysis as well as "returns" from a car of grapes treated with SO_2. Previous to the shipping of this car, Mr. Wheeler had treated a number of car-loads of wine grapes intended for short distance shipments and had obtained very encouraging results. The manner of application of SO_2 used by him in these treatments was practically identical with that used in most of the tests at Davis (described on pp. 123 and 124). This car, which was distinctly an experimental shipment to New York, contained a number of varieties in variable condition, as shown in table 13. After treatment, the car was kept closed for about 30 minutes. It was then entered and samples removed for analysis from the positions indicated in table 13.

The data presented in table 13 show that similar results, with regard to the quantity of SO_2 absorbed by the grapes and the uniformity of distribution, may be obtained in the treatment of car-loads as in the smaller air-tight rooms used for the experimental work at Davis. Furthermore, when account is taken of the condition of some of these grapes (Alicante Bouschet, Carignane, and Lenoir especially), which was such as to preclude shipment for more than a very short distance in the regular refrigerator car, the quality of the grapes when sold in New York, 18 days after treatment, and the price received, indicate that the treatment was of considerable value in lengthening the period of utility of these grapes.

TABLE 13

RESULTS OBTAINED FROM A CAR-LOAD OF GRAPES TREATED WITH SO_2 BY MR. J. H. WHEELER, ST. HELENA, CALIFORNIA

Variety	Condition when loaded	Position in car			Mgs. SO_2 absorbed per kilo. of grapes	Condition of grapes when sold in N. Y. 18 days after treatment*	Price received*
		Stack	Row	Layer			
Green Hungarian....	Very soft berries. Many berries broken. (Balling 18.3)°	2	3	1	104.2		
		2	3	5	94.2		
		3	5	1	75.0		
		3	5	5	70.0		
		6	3	1	77.8		
		6	3	5	90.0	Very soft berries. Mostly good color, fair pack.	.90
		10	3	1	108.4		
		10	3	5	96.6		
		13	2	1	89.6		
		13	3	8	75.2		
		Middle of car					
		14	3	8	96.0		
Alicante Bouschet..	Had been held on platform a week before loading. Berries soft, slight mold, color good.					Soft berries. Good color.	2.60
Carignane..................	Had been held on platform a week before loading. Some berries raisined, slight mold, slightly off color (reddish).					Slightly raisined. Slightly reddish color.	2.25
Lenoir..........................	Had been held on platform a week before loading. Berries soft, slight mold, color good.					Good color. Very small bunches.	2.25
Petite Sirah..............	Had been held on platform a few days before loading. Berries soft, color good.					Very soft berries. Mostly good color.	1.90

* Report to J. H. Wheeler by the Earl Fruit Co.

SUMMARY

1. Of the commoner preservatives, sulfur dioxide, boric acid, formic acid, formaldehyde, benzoate of soda, and salicylic acid, sulfur dioxide alone is promising as a preservative for fresh grapes.

2. Sulfur dioxide in suitable concentrations prevents or retards the activity of all micro-organisms usually concerned in the spoiling of grapes.

3. A small quantity of sulfur dioxide decreases the rate of respiration in grapes.

4. With a suitable concentration of SO_2 uniformly applied to the grapes in sealed containers, it has been found possible to prevent the loss of sugar and the accumulation of alcohol almost indefinitely.

5. Uniformity of distribution of the SO_2 throughout the grapes in the sealed containers is absolutely essential for success.

6. The type and size of container, so long as it is air-tight and not easily corroded by acid, is of little or no consequence.

7. The SO_2 may be applied as a gas in air, or the grapes in the container may be immersed in a water solution of the gas or in a water solution of potassium or sodium metabisulfite for a definite length of time.

8. The treatment of grapes with SO_2 in sealed containers increases the permeability of the cells, so that the color, tannins, and other substances are released. This renders the fruit unsuitable for table use. For manufacturing purposes where the release of color and tannins into the juice is not objectionable, the grapes are almost equal to fresh fruit.

9. Through the uniform application of very small quantities of SO_2 to grapes in open containers, e.g. loaded cars, it has been found possible to double the period of time elapsing before spoiling with no injury to quality. Grapes treated in this way were in good condition for eating fresh.

10. The rate of absorption of SO_2 by grapes is influenced by (*a*) concentration of SO_2 in the atmosphere, (*b*) time of exposure, (*c*) temperature of the grapes, (*d*) maturity of the grapes, and (*e*) physical condition (soundness) of the grapes.

11. A uniform distribution of a suitable concentration of SO_2 without injury to quality may be obtained in grapes arranged as in loaded cars, when the following requirements are met: (*a*) a sufficient SO_2 supply and air flow to displace the air in the car with a uniform SO_2 air mixture within two or three minutes, (*b*) the SO_2 air mixture must be cool before being driven into the car, and (*c*) the equipment must be capable of maintaining this flow of SO_2 in air for from 10 to 30 minutes according to the concentration of the mixture used.

12. It was found that with a 2 or 3 per cent SO_2 concentration in the air, about twenty minutes was required to cause sound grapes to absorb 50 to 100 mgs. per kilo. With a 4 to 6 per cent SO_2 concentration in the air the time required was about ten minutes.

13. It was found that 50 mgs. of SO_2 per kilo. of grapes is sufficient approximately to double the keeping period and that 100 mgs. does not injure the color, texture or flavor of the grapes.

14. It was found impossible to treat grapes successfully by burning the sulfur inside the closed room or car.

15. The results obtained from an experimental car-lot shipment of grapes by Mr. J. H. Wheeler indicate that the results obtained in these experiments may be applied to commercial practice.